

Thermoelectric Properties of n-type Polycrystalline $\text{Bi}_x\text{Sb}_{1-x}\text{Te}_3$ Alloys

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Abstract

$(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ ($0.5 \leq x \leq 0.7$) polycrystalline samples were synthesized using a combination of melting and powder metallurgy techniques. The samples were hot pressed in graphite dies and cut perpendicular and parallel to the pressing direction. Samples were examined by microprobe analysis to determine their atomic composition. The thermoelectric properties were measured at room temperature in both directions. These properties include Seebeck coefficient, thermal conductivity, electrical resistivity, and Hall effect. The thermoelectric figure-of-merit, ZT , was calculated from these properties. The best ZT was ~ 0.5 , given by annealed $(\text{Bi}_{0.7}\text{Sb}_{0.3})_2\text{Te}_3$. Selected samples were also annealed at various temperatures in an attempt to optimize ZT . The annealing substantially impacted the thermoelectric properties due to a combination of improved crystallinity and changes in defect concentration. These materials could potentially be incorporated into advanced thermoelectric unicouples for a variety of power generation applications.

Introduction

The best thermoelectric materials are semiconductors which limit the movement of heat conducting phonons while permitting the free flow of negatively charged electrons or positively charged holes. The quality of a thermoelectric material is described by a dimensionless figure-of-merit, ZT , which depends on three measurable properties: electrical resistivity (ρ), Seebeck coefficient (S), and thermal conductivity (α). ZT is calculated using the relation $ZT = TS^2/\alpha\rho$, where T is the absolute temperature of the material [1]. When comparing materials that have similar thermal conductivities, it is also appropriate to speak in terms of the power factor (S^2/ρ).

In an effort to generate power more efficiently from thermal gradients, the Jet Propulsion Laboratory Thermoelectrics Group is developing a segmented uncouple using advanced materials. A segmented uncouple is a uncouple whose legs are made up of more than one material. This allows parts of the legs to be optimized for specific temperature ranges. The materials for each leg are carefully placed, in order, in a graphite die, where they are pressed together to form a solid leg. The fact that the materials are pressed together introduces a new requirement. Not only do the materials need to have good thermoelectric properties, they need to have them in the direction parallel to the pressing. For most of the materials, this is not a problem, since they have cubic lattices and are isotropic; they have all been optimized. The cold n type material, however, has yet to be finalized. $\text{Bi}_2\text{Te}_{2.95}\text{Se}_{0.05}$ is currently being used, but it is thought that a better material can be found. $\text{Bi}_2\text{Te}_{2.95}\text{Se}_{0.05}$ has very attractive properties, but not in the right direction, due to anisotropy.

A replacement for $\text{Bi}_2\text{Te}_{2.95}\text{Se}_{0.05}$ could possibly be found among the solid solutions of Bi_2Te_3 - Sb_2Te_3 . Traditionally,

some of the best thermoelectric materials have been made from $(\text{Bi,Sb})_2\text{Te}_3$ compounds. In polycrystalline form, meaning made up of many small crystal grains instead of one large crystal, $(\text{Bi,Sb})_2\text{Te}_3$ can be either p or n type. Compounds that are mostly Sb_2Te_3 are p type, and have high ZT s. The p type, Sb rich $(\text{Bi,Sb})_2\text{Te}_3$ alloys have been thoroughly investigated, while the n type alloys have not. The p-n transition occurs at roughly 40 mol% Bi_2Te_3 [2]. Like BiTeSe , $(\text{Bi,Sb})_2\text{Te}_3$ is anisotropic; that must be taken into account when optimizing the material.

Optimized thermoelectrics will have a high Seebeck coefficient, and low electrical resistivity and thermal conductivity, resulting in a high ZT . This is difficult to accomplish, because all three properties are dependant on the carrier concentration; improvements cannot be made without some sacrifice. By carefully controlling the carrier concentration, though, materials can be improved. Annealing can be used to alter the defect concentration of the materials, thereby altering the carrier concentration. The trade off is that annealing can also promote grain growth, which increases thermal conductivity. Therefore, in order to optimize the $(\text{Bi,Sb})_2\text{Te}_3$ compounds, the effects of annealing must be understood.

Alloys are synthesized by melting materials in a vacuum-sealed ampoule. The resulting ingot is ground into a fine powder and then pressed into a cylindrical pellet. The thermoelectric properties are then measured. This is repeated for the annealed samples. The results indicate that the best n type material tested is $\text{Bi}_{1.4}\text{Sb}_{0.6}\text{Te}_3$, which has a power factor of $19.7 \mu\text{W}/^\circ\text{K}^2\text{cm}$ when annealed after pressing. Annealing was found to alter both the concentration and the nature of the defects in the material. While not resulting in a better material, this research may be applied towards the optimization of other, similar materials.

Materials and Methods

To prepare the $(\text{Bi,Sb})_2\text{Te}_3$ alloys, high purity (99.999% pure or better) Bi, Sb, and Te are weighed and placed in a quartz ampoule. The ampoule is vacuum-sealed at 10^{-5} torr using a diffusion pump and a hydrogen/oxygen torch. The ampoule is then placed in a 700°C furnace, where the materials will melt and mix for at least 24 hours. It is then removed from the furnace and immediately water quenched, to ensure that the entire sample is homogeneous. The resulting ingot is ground using an agate mortar and pestle, then passed through a 125μ sieve. The powder is then hot pressed for 1.5 hours in an argon environment at 535°C at $\sim 18,000$ psi using a graphite die, producing a cylindrical pellet with a diameter of 12mm .

An initial measurement of the Seebeck coefficient is performed on the pellet. Seebeck is determined by measuring the voltage across the sample due to a thermal gradient. The thermal gradient is created by placing a room temperature plate on one side of the sample, and a water-cooled plate on

the other. The temperature and voltage are measured at the same point using thermocouples. The Seebeck coefficient is calculated using $\Delta V = S\Delta T$, where ΔV is the voltage difference, S is the Seebeck coefficient, and ΔT is the temperature difference. Give an example of what kind of ΔT you use for the measurement.

Next, the thermal conductivity is measured. The pellet is stacked on top of a quartz reference sample of the same size, with a thermocouple sandwiched in between. The stack is then placed in a thermal gradient created by a heater and a water-cooled plate. The samples are wrapped in insulation to minimize lateral heat losses. After the stack has thermally equalized, temperatures are measured using the hot, cold and middle thermocouples. The thermal conductivity is calculated using the following equation,

$$\lambda_{\text{Sample}} = \lambda_{\text{Reference}} \times L_{\text{Sample}} / L_{\text{Reference}} \times \Delta T_{\text{Reference}} / \Delta T_{\text{Sample}},$$

where λ is the thermal conductivity, L is pellet length, and ΔT is the temperature difference across the material. The thermal conductivity of quartz is roughly 13.8 mW/cm²K. The process is repeated, flipping the stack so the heat is flowing in the opposite direction, and the two resulting measurements are averaged.

After the Seebeck coefficient and thermal conductivity of the pellet have been measured, the pellet is then cut into 1 mm thick slices both parallel and perpendicular to the pressing direction. This allows properties to be measured in both directions, so anisotropy can be examined; it is also a requirement for the Hall effect measurement equipment. After the disks and plates have been cut, the Seebeck coefficient is measured again, using the methods previously outlined.

The charge transport properties are measured using the Hall effect. The measurements are made using the van der Pauw method [3], which utilizes four probes evenly spaced around the sample. Electrical resistivity and Hall constant are measured at the same time, from which the carrier mobility and carrier concentration are calculated.

For certain samples, high temperature measurements were performed. High temperature Seebeck and Hall effect measurements are done in a vacuum environment, over the expected operating temperature range for these materials, room temperature to roughly 250° C. High temperature thermal conductivity measurements were not possible, because of equipment failure.

The effects of annealing were also investigated. Some samples were annealed after being pressed and cut, while others were annealed as ground powders, before pressing. The samples to be annealed are vacuum-sealed in quartz ampoules, and heated in a furnace at a specific temperature for 48 hours. Thermoelectric properties are then measured.

To determine if any stoichiometric deviation occurred, and to make sure the samples were homogenous, certain materials underwent microprobe analysis.

Results and Discussion

For this research, a total of fourteen samples were made from seven different ingots.

Tables 1 and 2 show the room temperature properties measured both parallel and perpendicular to the pressing direction, respectively. The values for thermal conductivity

were obtained by measuring parallel to the pressing direction; these values are used in figure of merit calculations both parallel and perpendicular to the pressing. Accurate perpendicular thermal conductivity measurements were not possible due to the shape of the pellet.

High temperature measurements were limited to Seebeck coefficient and Hall effect; equipment failure prevented high temperature thermal conductivity measurements. Therefore, the results summarized in figure 1 are in terms of power factor, instead of figure of merit.

Microprobe analysis of the first five alloys showed that they are indeed the desired compositions, and are homogenous.

Composition

The first five samples were made to determine the optimal n type composition for (Bi,Sb)₂Te₃. From the observed data, it can be seen that as the Bi₂Te₃ concentration increases, both the Seebeck coefficient and the electrical resistivity decrease (as measured parallel to the pressing direction.) The 47% decrease in resistivity compensates for the 11% decrease in Seebeck, resulting in a power factor that increases with the Bi₂Te₃ concentration, as seen in figure 2.

The power factor plateaus between 60% and 70% Bi₂Te₃; this agrees with previously published research [2]. When all five compositions were annealed for 48 hours at 550° C, the plateau disappears, and the power factor reaches a maximum at 70% Bi₂Te₃. Based on these results, Bi_{1.4}Sb_{0.6}Te₃ was chosen for further investigation.

Out of the five different compositions tested, the best results were obtained by Bi_{1.4}Sb_{0.6}Te₃, which was annealed after being pressed. The room temperature power factor for this sample, 19.7 μW/°K²cm, is greater than that of Bi₂Te_{2.95}Se_{0.05}. However, since Bi₂Te_{2.95}Se_{0.05} has a much lower thermal conductivity than the non-annealed Bi_{1.4}Sb_{0.6}Te₃, and annealing is observed to increase thermal conductivity, it can be assumed that Bi₂Te_{2.95}Se_{0.05} has a better figure of merit. This was not verified because an accurate thermal conductivity measurement of the thin annealed sample could not be performed.

Annealing

As previously stated, annealing is expected to alter the defect concentration of (Bi,Sb)₂Te₃ alloys. These defects influence both the thermal and the electronic properties of the material. This is illustrated by the annealed powder results. Tables 1 and 2 show that as the annealing temperature for the Bi_{1.4}Sb_{0.6}Te₃ powders is increased, the thermal conductivity increases, except for the 580°C anneal, which breaks the trend. These values for thermal conductivity can be broken into two parts, lattice and electronic. Electronic thermal conductivity, λ_e , can be calculated with the relation $\lambda_e = L\sigma T$, where σ is electric conductivity, T is absolute temperature, and L is the Lorenz number. The lattice thermal conductivity is simply the difference between λ_e and the overall thermal conductivity. Figure 3 shows these two thermal conductivities plotted as functions of annealing temperature. The lattice thermal conductivity varies with temperature, while the electronic thermal conductivity shows only a slight decrease.

| (Bi _x Sb _{1-x}) ₂ Te ₃ (x=...) | Anneal Temp. (°C) | Thermal Conductivity (mW/cm ² K) | Resistivity (mΩ cm) | Carrier Mobility (cm ² /Vs) | Carrier Concentration (cm ⁻³) | Seebeck Voltage (μV/°K) | Power Factor (μW/°K ² cm) | ZT |
|--|-------------------------|---|------------------------|--|---|-------------------------------|--|-----|
| 50% | not annealed | 9.99 | 2.167 | 128.31 | 2.25E+19 | 137.8 | 8.77 | .26 |
| 55% | | 11.06 | 1.614 | 123.80 | 3.13E+19 | 133.0 | 10.96 | .30 |
| 60% | | 11.42 | 1.301 | 134.70 | 3.57E+19 | 130.0 | 12.99 | .34 |
| 65% | | 10.49 | 1.216 | 133.11 | 3.86E+19 | 128.2 | 13.51 | .39 |
| 70% | | 11.91 | 1.141 | 149.17 | 3.67E+19 | 122.9 | 13.25 | .33 |
| 50% | 550° | 9.99 | | | | | | |
| 55% | | 11.06 | 2.692 | 129.82 | 1.79E+19 | 192.6 | 13.78 | .37 |
| 60% | | 11.42 | 6.143 | 133.63 | 7.61E+18 | | | |
| 65% | | 10.49 | 1.870 | 114.33 | 2.92E+19 | 181.8 | 17.67 | .51 |
| 70% | | 11.91 | 1.893 | 148.07 | 2.23E+19 | 192.9 | 19.66 | .50 |
| 70% | 531° | 13.60 | 0.986 | 145.50 | 4.36E+19 | 123.8 | 15.55 | .34 |
| 70% | 539° | 14.56 | 0.995 | 146.37 | 4.29E+19 | 120.1 | 14.49 | .30 |
| 70% | 560° | 15.20 | 0.996 | 158.38 | 3.96E+19 | 121.8 | 14.91 | .29 |
| 70% | 580° | 12.72 | 1.031 | 136.69 | 4.44E+19 | 128.5 | 16.02 | .38 |

Table 1: Room Temperature Properties of n-type BiSbTe Alloys Measured Parallel to Pressing Direction

| (Bi _x Sb _{1-x}) ₂ Te ₃ (x=...) | Anneal Temp. (°C) | Thermal Conductivity (mW/cm ² K) | Resistivity (mΩ cm) | Carrier Mobility (cm ² /Vs) | Carrier Concentration (cm ⁻³) | Seebeck Voltage (μV/°K) | Power Factor (μW/°K ² cm) | ZT |
|--|-------------------------|---|------------------------|--|---|-------------------------------|--|-----|
| 50% | not annealed | 9.99 | 1.731 | 134.59 | 2.68E+19 | 146.1 | 12.33 | .37 |
| 55% | | 11.06 | 1.335 | 144.37 | 3.24E+19 | 133.8 | 13.42 | .36 |
| 60% | | 11.42 | 1.112 | 144.12 | 3.90E+19 | 133.3 | 15.97 | .42 |
| 65% | | 10.49 | 0.999 | 149.18 | 4.19E+19 | 127.7 | 16.31 | .47 |
| 70% | | 11.91 | 0.949 | 165.23 | 3.99E+19 | 128.6 | 17.43 | .44 |
| 50% | 550° | 9.99 | | | | | | |
| 55% | | 11.06 | 3.508 | 152.78 | 1.17E+19 | 164.9 | 7.75 | .21 |
| 60% | | 11.42 | | | | 221.4 | | |
| 65% | | 10.49 | 2.372 | 144.89 | 1.82E+19 | 149.4 | 9.41 | .27 |
| 70% | | 11.91 | 2.494 | 155.26 | 1.61E+19 | 166.7 | 11.14 | .28 |
| 70% | 531° | 13.60 | 0.916 | 151.18 | 4.51E+19 | 126.1 | 17.37 | .38 |
| 70% | 539° | 14.56 | 0.904 | 154.61 | 4.47E+19 | 125.3 | 17.38 | .36 |
| 70% | 560° | 15.20 | 0.878 | 143.94 | 4.95E+19 | 126.6 | 18.25 | .36 |
| 70% | 580° | 12.72 | 0.869 | 149.79 | 4.80E+19 | 131.8 | 20.00 | .47 |

Table 2: Room Temperature Properties of n-type BiSbTe Alloys Measured Perpendicular to Pressing Direction

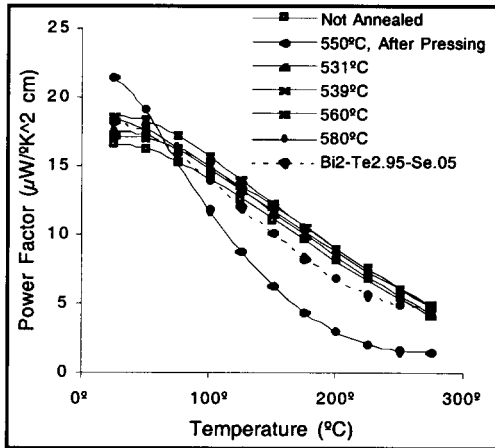


Figure 1: High Temperature Power Factor Results

The variations in lattice thermal conductivity could be due to changes in grain size, or changes in the concentration phonon scattering defects, or both [4]. It is less likely that the changes in thermal conductivity are due to grain growth since, out of the four temperatures, the lowest thermal conductivity occurs at the highest temperature, where the greatest grain growth would be expected. Therefore, it

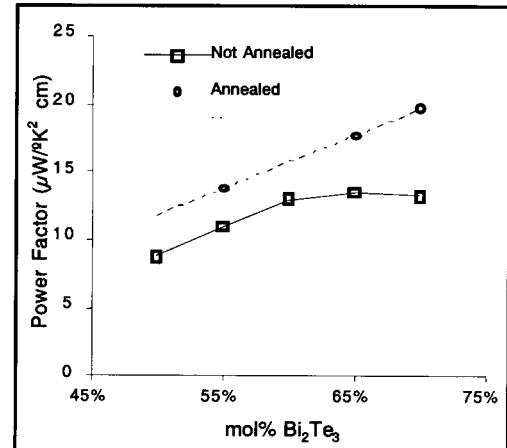


Figure 2: Power Factor vs. Composition, measured parallel to pressing direction, before and after anneal (post pressing.)

appears that annealing reduces the concentration of phonon scattering defects in the lattice.

Annealing also affects the electronic properties of the materials. When the electrical resistivity is plotted as a

function of carrier concentration for the annealed powders (figure 4), a trend becomes evident. This shows that annealing alters the concentration of defects, and those defects are electrically active.

Thus, it can be seen that annealing alters both the concentration of defects, as well as their nature.

In addition to influencing the defects, annealing also promotes grain growth. This is indicated by the increasing anisotropy illustrated in figure 5. The anisotropy of $(\text{Bi,Sb})_2\text{Te}_3$ is due to its rhombohedral crystal structure. The difference between parallel and perpendicular measurements is the greatest when dealing with a single crystal. As the grains in a polycrystalline sample grow bigger, they approach the properties of a single crystal, and the anisotropy increases. Figure 5 shows that this is the case with the annealed powders.

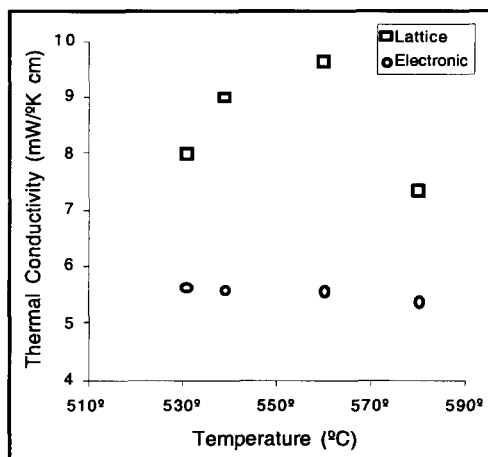


Figure 3: Lattice/Electronic Thermal Conductivity vs. Anneal Temperature

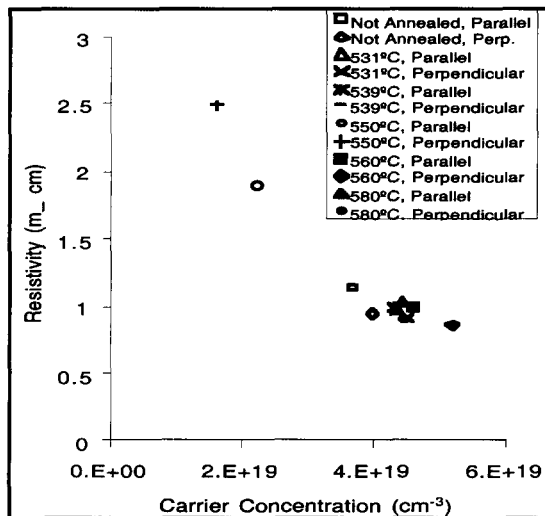


Figure 4: Electrical Resistivity vs. Carrier Concentration
High Temperature

Since these materials are to be used over a range of temperatures, they cannot be judged solely on their room temperature performance. Figure 1 shows the power factor for all $\text{Bi}_{1.4}\text{Sb}_{0.6}\text{Te}_3$ samples, as well as the $\text{Bi}_2\text{Te}_{2.95}\text{Se}_{0.05}$ goal. It is interesting to note that the sample with the best room temperature properties, the one annealed after pressing, has the worst high temperature performance. This could indicate a correlation between grain size and high temperature

performance. In general, the rest of the samples follow the same trend, which is slightly better than that of $\text{Bi}_2\text{Te}_{2.95}\text{Se}_{0.05}$. This is not enough information to make a firm statement, since high temperature thermal conductivity measurements were not possible.

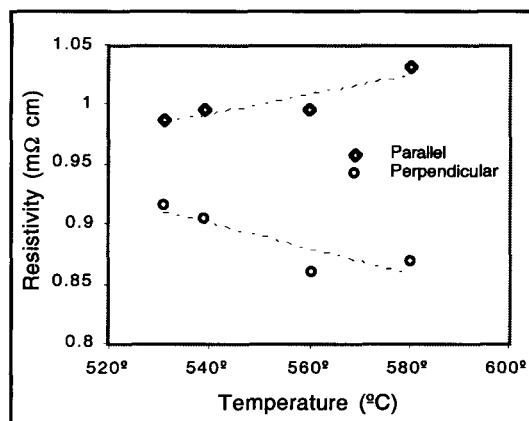


Figure 5: Electrical Resistivity vs. Anneal Temperature

Conclusions

- Of the compounds tested, $\text{Bi}_{1.4}\text{Sb}_{0.6}\text{Te}_3$ had the best thermoelectric qualities, with a room temperature figure of merit of .33, which rose to .5 after annealing. This is not better than $\text{Bi}_2\text{Te}_{2.95}\text{Se}_{0.05}$.
- Annealing has the effect of altering the nature and concentration of defects, as well as promoting grain growth.
- Annealing alone does not seem to significantly alter the behavior of the power factor at high temperature.

Although no “miracle materials” were discovered, the techniques investigated, namely annealing, can be applied to similar materials, such as $\text{Bi}_2\text{Te}_{2.95}\text{Se}_{0.05}$.

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